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(71) Applicant: COURTAULDS FIBRES (HOLDINGS) LIMITED [GB/GB]; 50 George Street, London W1A 2BB (GB).

(72) Inventors: SELLARS, Alan; 2 Trinity Close, Goxhill, South Humberside DN19 7NN (GB). QUIGLEY, Michael, Colin; 41 Bonneville Close, Meriden CV5 9QH (GB).

(74) Agent: NEWBY, John, Ross; J.Y. & G.W. Johnson, Furnival House, 14-18 High Holborn, London WC1V 6DE (GB).

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(54) Title: MONITORING CONCENTRATION OF DOPE IN PRODUCT MANUFACTURE

(57) Abstract

Monitoring means are provided to control the concentration of a dope of cellulose/amine oxide/water solution for use in the manufacture of continuous filaments of solvent-spun cellulose. The dope may be formed by preparing a mixture of cellulose amine oxide solvent and water, and heating the mixture to drive off excess water to form the hot dope solution which is then passed to a die assembly which forms strands from the dope which are then further processed to make the filaments of solvent-spun cellulose. The concentration of the solution is monitored by measurement of its refractive index and maintenance of the refractive index within specified limits by adjustment of the water content ensures that the dope concentration is such as to produce a good product.

Monitoring Concentration of Dope in Product Manufacture

This invention relates to the monitoring of the concentration of the components of a dope used in the manufacture of a cellulose product (e.g. cellulose fibre) from a solution of cellulose in an organic solvent, particularly an amine oxide solvent and water. Cellulose manufactured in this manner is known as lyocell and will hereafter be referred to as solvent-spun cellulose or lyocell. The term "dope" as used herein refers to the solution of cellulose in an aqueous tertiary amine oxide.

The invention particularly aims to provide a means to monitor the dope concentration before it is passed to be spun (e.g. into strands which are to be further treated to form desired filaments). The manufacture of lyocell cellulose filaments is described, for example, in U.S. Patent No. 4,416,698 the contents of which are incorporated herein by way of reference. This Patent discloses a method of producing cellulose filaments by dissolving the cellulose in a suitable solvent such as a tertiary amine N-oxide.

A hot solution of the cellulose i.e. dope, is extruded or spun through a suitable die assembly including a jet to produce strands of the dope which are passed into water to leach out the amine oxide solvent from the extruded strands to produce the desired extruded material.

The production of artificially formed filaments of material by extruding or spinning a solution or liquid through a spinnerette to form the filaments is, of course, well known. Initially, relatively small numbers of individual filaments were prepared, which filaments were individually wound up for use as continuous filament material. This meant that the number of continuous filaments which needed to be produced was essentially dictated by the number of filaments which could be individually wound either before or after drying.

However, if fibre is produced as a tow, or if fibre is produced as a staple fibre, then different criteria apply to the number of filaments which can be produced at any one time. A tow essentially comprises a bundle of essentially parallel filaments which are not handled individually. Staple fibre essentially comprises a mass of short lengths of fibre. Staple fibre can be produced by the cutting of dry tow or it can be produced by forming a tow, cutting it whilst still wet, and drying the cut mass of staple fibre.

Because there is no need to handle individual filaments in the case of a tow product or a staple product, large numbers of filaments can be produced simultaneously.

In order that the dope can be spun readily into the desired end product it is necessary to ensure that concentration of the three phase dope solution i.e. cellulose amine oxide and water, is constrained between predetermined limits. Thus at the beginning of the manufacturing process amine oxide, water and shredded cellulose together with a stabiliser such as propyl gallate are mixed in a pre-mixer at elevated temperature, the pre-mixed solution so obtained may be passed through a thin film evaporator to apply conditions of increased temperature and reduced pressure so as to reduce the water content of the mixture and form a hot viscous solution or dope. The dope from the thin film evaporator is passed to the die assembly to form strands of dope which are then passed through a spin bath and then to a further water bath to leach out the amine oxide solvent. The resulting product (which can be a tow of filaments) is then passed to further processing stages, e.g. finishing operations, drying and crimping and/or storage.

The amine oxide leached out of the strands is preferably recycled. Thus, to recover the amine oxide, the contents of the spin bath are passed to an evaporator to increase the amine oxide concentration to that desired for the original starting material. This amine oxide is then fed to the

pre-mixer with more cellulose to start the cycle again. Moreover, the amine oxide/water from the further water bath can be passed to the spin bath.

It will be appreciated that the amine oxide/water/ cellulose concentrations in the dope need to be monitored to ensure that it is of the right strength to make a good product.

It is one aim, therefore, of the invention to provide monitoring means to check and to ensure that the amine oxide/water/cellulose concentration of the hot viscous dope is of the desired concentration before it passes to the die assembly. Preferably monitoring is followed by adjustment of the composition to the desired concentrations.

It is a further aim of the invention to provide monitoring means to check the concentration of amine oxide drawn off from the further water bath.

It is a yet further aim of the invention to provide monitoring means to check and to ensure that the concentration of amine oxide to be recycled is of the desired level for feeding back to the pre-mixer. The invention is based on the surprising realisation that if the refractive index of the three-phase solution, i.e. cellulose, amine oxide and water, is maintained within relatively narrow predetermined limits, i.e. if the three constituents are controlled so that the refractive index of the dope stays within those limits, a good product can be obtained from the dope. If the concentration of the dope changes so that the refractive index of the dope is allowed to go outside those limits, a satisfactory product may not be obtained. The reasons for this are not fully understood and it is indeed surprising that concentration of a three-phase solution can be controlled in this manner.

In one aspect, therefore, the inventi n provides a method of monitoring the concentration of a solution for use in the

manufacture of at least one elongate member of solvent-spun cellulose which is characterised in that the cellulose is dissolved in amine oxide and water to form a hot dope solution, the dope solution is passed to a die assembly to be extruded to form the elongate member, the elongate member is passed through a spin bath containing a solution of amine oxide and water in which a portion of the amine oxide in the elongate member is leached into the spin bath and the elongate member is then passed through a water bath in which the remainder of the amine oxide is leached out, the refractive index of at least one of the solutions being measured and the concentration of the solution being adjusted if its refractive index varies from a predetermined value by more than a predetermined amount.

Suitably the refractive index of the dope solution is measured prior to its being extruded and the concentration of the dope is adjusted if the refractive index falls outside the range 1.4890 to 1.4910 at 60°C.

Preferably, the amine oxide, water and cellulose are mixed in a pre-mixer and the solution so obtained is passed through a thin film evaporator to reduce the water content to form the hot viscous dope.

In another aspect the invention provides an apparatus for the monitoring of the concentration of a solution for use in the manufacture of at least one elongate member of solvent-spun cellulose, which comprises means to form a hot dope solution from a mixture of cellulose, amine oxide and water, an extruder to form at least one continuous elongate member from the hot dope solution, a spin bath to contain a solution of amine oxide and water through which the elongate member can be passed, a water bath to contain a solution of amine oxide and water through which the elongate member can be passed and monitoring means, the monitoring means comprising means to measure the refractive index of at least one of the solutions.

The amine oxide solvent will preferably be a tertiary amine N-oxide. The source of cellulose may be of, for example, shredded paper or shredded wood pulp. A small amount of stabiliser e.g. propyl gallate, may also be included in the pre-mixer, e.g. from 0.1 to 2% by weight of the ingredients.

The refractive index monitoring means may be a manual, i.e. batch, measurement in which samples of the hot dope solution are extracted at time intervals and taken to an appropriate instrument for measurement or the means may be a continuous measuring means installed in the production line. A suitable instrument for in-line measurement is, for example, a Process Refractomer type PR-01 supplied by K-Patents.

It will be appreciated that the refractive index of the dope varies with temperature. It is, therefore, necessary to take temperature into account and, in the batch-testing process, it is preferred that the measurement be carried out at 60°C. Thus the hot sample is allowed to cool to that temperature before the measurement is taken. If in-line monitoring is carried out, then it is necessary that the monitoring means also measures the temperature of the dope and the refractive index measuring means is calibrated to compensate for temperature.

We have found that dope solutions whose refractive index at 60°C lies in the range 1.4890 to 1.4910 are satisfactory for use and result in satisfactory products. As indicated above, in the manufacture of solvent-spun cellulose filaments, amine oxide leached out of the strands may be recycled and, after any necessary concentration adjustment, used to dissolve more cellulose. Moreover, the hot strands emerging from the extruder die are passed through a spin bath in which a mixture of water and cellulose is recirculated and partial leaching out of the amine oxide from the strands commences. From the spin bath the strands then pass to the water bath where the leaching out process is completed. Amine oxide from the water bath may, therefore, be circulated to the spin bath.

The amine oxide drawn off from the water bath can be passed through an in-line monitoring station where its concentration is continuously monitored as it is passed to the spin bath.

Amine oxide can be drawn off from the spin bath and its concentration, i.e. water content, adjusted to the level required for re-use in an initial pre-mixing stage to dissolve more cellulose and the amine oxide of adjusted concentration can then be passed through an in-line monitoring station where its adjusted concentration is continuously monitored.

Specific embodiments of the invention will now be further described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a ternary diagram showing cellulose in N-methylmorpholine N-oxide and water;

Figure 2 is a diagrammatic illustration of the refractive index measurement means;

Figure 3 is a diagrammatic representation of the various stages in the manufacture of a continuous tow of solvent-spun cellulose fibres, i.e. lyocell;

Figure 4 is a graph showing the variation with concentration of refractive index of solutions of amine oxide and water at 60°C; and

Figure 5 shows the variation with temperature of refractive index of a 77.5% amine oxide, 22.5% water solution.

The ternary diagram of Figure 1 shows clearly that for cellulose to be in solution in an amine oxide:water phase, the proportions of the three ingredients must be kept within closely-defined and narrow concentration ranges.

In Figure 2, the basic principle of the preferred refractive index measurement is illustrated. A prism 10 whose face 11 is wetted by the solution whose concentration is to be measured is subjected to a beam of light rays 12 from a source 13, the rays being at a multiplicity of angles to the surface 11. Some of the rays 12A will be refracted and pass through face 14 of the prism. Others 12B of the rays will be reflected and pass through face 15 of the prism to impinge on a receiver 16. Part 16A of the receiver will be in shadow, receiving no light rays, and part 16B will be receiving the light rays 12B. The position of the boundary between parts 16A and 16B will be determined by the concentration of any particular solution. Thus the refractive index measuring device can be pre-calibrated using solutions of known concentration. By means of photocell sensors in the receiver 16, the boundary between the shadow region and the remainder can be monitored and using a pre-programmed microprocessor or chip 17, any variations of concentration beyond predetermined and pre-set values will trigger a response, which can activate compensating means automatically or manually, as desired, to correct the concentration deficiency.

In Figure 3, amine oxide and water are introduced into a pre-mixer 30 via inlet 31 and shredded cellulose, stabiliser and water are introduced into the pre-mixer via inlet 32. The mixture so formed is passed through a thin film evaporator 33 where the water concentration is reduced and a hot dope is produced. For example, a 78/22 w/w amine oxide/water mixture and a 94/6 w/w cellulose/water mixture may be introduced into the pre-mixer in proportions to give a 13/19/68 w/w cellulose/water/amine oxide mixture. That mixture is passed to the thin film evaporator 33 where the mixture is heated and evaporated and the water content is reduced so that the solution (dope) formed therein there is 15/9/76 w/w cellulose/water/amine oxide solution.

From the film evaporator 33 the hot dope solution is passed to a spinnerette 34 where it is spun into continuous

strands 35 of fibres. As the hot strands 35 emerge from the spinnerette 34, they pass through an air gap and into a spin bath 36 in which a mixture of water and amine oxide is recirculated. At the start up, there may be no amine oxide in the spin bath but its proportion to water may rise to about 25% by weight. From spin bath 36 the strands pass via roll 37 through a wash bath 38. The strands passing through the wash bath may be, for example, up to 12 to 14 inches (30 to 35 cms) wide. In the wash bath 38 the amine oxide not leached out in the spin bath 36 is washed out of the strands and the tow 39 emerging from the water bath is of solvent-spun cellulose, i.e. lyocell.

From the wash bath 38, the tow 39 is passed for finishing operations, e.g. through a bath to add finishing chemicals to the fibre, through a drier and to crimping and/or storage and/or cutting means to reduce the filaments to staple fibre lengths.

To ensure that the cellulose/water/amine oxide dope solution passing from the thin film evaporator 33 to the spinnerette 34 is of the required concentration, a valve 50 is provided between the evaporator and spinnerette so that samples of the solution can be drawn off for testing. 100g (3.5 ounces) samples are withdrawn at suitable time intervals. The dope is a hot and very viscous solution at this stage (e.g. it may have a viscosity of 1 to 5000 Pascal seconds at 105°C.) and it is found convenient to wrap the samples in polyester film to transport them to a refractive index measuring station indicated at 40 in Figure 3. A 5g (0.18 ounce) 1mm (0.04 inch) thick portion of the 100 g sample is placed in the refractive index measuring instrument 40, which is maintained at 60°C. After two minutes to allow the sample temperature to reach 60°C, its refractive index is measured. The instrument is pre-calibrated as described above. For the 15/9/76 cellulose/water/amine oxide solution, the refractive index measurement should be 1.4895. At a value of 1.4860 a significant proportion of the cellulose fibres are out of

solution and at a value of 1.4930 crystallisation is taking place. Thus, as indicated above, limits of 1.4890 to 1.4910 can be set as acceptable. Any reading outside these limits means that the feed to the pre-mixer and/or the evaporator conditions requires adjustment.

During start up of the manufacturing process it may be necessary to take refractive index readings of the hot dope once every 1 to 10 minutes but during normal operating conditions a measurement once every hour or up to 2 hours may be found to be satisfactory. Of course, if problems, e.g. with the feed materials, are being experienced, it will be necessary to increase the frequency of monitoring.

The manufacturing process illustrated in Figure 3 also includes two in-line refractive index monitoring stations.

Water is fed to the wash bath 38 via a line 100 and a valve 101. From the bath 38 the water, with some amine oxide in it, is passed to a circulation tank 102. The water-amine oxide in tank 102 is then pumped by pump 103 into line 104. The water/amine oxide then passes to the spin bath 36 via a line 105. Excess water and amine oxide from the spin bath 36 is recycled into the tank 102 via a line 106. A refractive index meter 107 monitors the water/amine oxide ratio in the line 104 and as the concentration of amine oxide in the line increases, the valve 101 is opened further (via connection 108, 109) to increase the water flow and reduce the amine oxide concentration.

Excess liquid in the tank 102 is passed to solvent recovery at 110.

If required more than one line producing fibre - e.g. line 111 can feed into the tank 102. Only the wash tank 112 and water line 113 of the line 111 is shown, but it is otherwise the same as 34-39.

The refractive index meter at 107 monitors the amine oxide/water concentration passing from tank 102 to the spin bath 36. Again, the meter 107 is pre-calibrated using suitable concentrations of amine oxide/water solutions and for a solution passing to the spin bath an amine oxide/water ratio of, say, 25:75 w/w could preferably be maintained. The refractive index of such a solution should be 1.3676 at 60°C. The refractive index measuring device is connected to a microprocessor unit 120. This can be pre-set such that any refractive index measurement outside the range of, say, 1.3644 to 1.3708 at 60°C triggers an adjustment to the valves such as valve 101 supplying water to the water bath 38. By this means the water/amine oxide concentration can be adjusted appropriately and automatically.

Figure 4 shows the linear change in refractive index with changing amine oxide concentration at 60°C. (It will be appreciated that a similar graph for the dope solution would be a 3-dimensional graph.).

It will be appreciated that the temperature of the amine oxide/water solution passing to the spin bath will not be at the 60°C. temperature at which the aforementioned dope refractive index measurements were carried out. A temperature compensation system must be used in calibrating the refractive index measurement for in-line operation. Figure 5 shows the Refractive Index:temperature relationship for a typical amine oxide/water (77.5/22.5 w/w) solution. Similar graphs can readily be plotted and the appropriate calibration carried out for any desired concentrations. The monitoring station, therefore, also measures the temperature of the amine oxide/water so that the correct calibration range is used by the instrument.

The second in-line monitoring station is shown at 44 in Figure 3.

The amine oxide/water solution taken from the tank 102

passes a valve 46 where more amine oxide may be added, if needed, and then through an evaporator 45, which may be a conventional three stage evaporator, where the concentration of the amine oxide to water is increased to the desired level for re-use of the amine oxide, i.e. to 78/22 w/w in the above example. From the evaporator 45, the amine oxide/ water passes monitoring station 44 where its refractive index is continuously monitored in the same manner as described with reference to station 107 above. The refractive index measurement for a 78/22 solution, when temperature compensated, as described above, should be 1.4624 at 60°C. If the value falls outside the range 1.4620 to 1.4628, a microprocessor 47, to which the refractive index measuring station is connected can operate valve 46 to admit additional amine oxide or can control the evaporator 45 conditions accordingly.

It will be appreciated that various embodiments can be changed without departing from the scope of the invention as defined in the following claims.

In particular, the desired amine oxide/water/cellulose proportions at the various stages of the process may be varied to meet differing manufacturing conditions and end-product specifications.

Moreover, if desired, more than one manufacturing line may share an in-line monitoring station with appropriate controls to determine which line at any time may require adjustment.

CLAIMS

1. A method of monitoring the concentration of a solution for use in the manufacture of at least one elongate member of solvent-spun cellulose, characterised in that the cellulose is dissolved in amine oxide and water to form a hot dope solution, the dope solution is passed to a die assembly (34) to be extruded to form the elongate member (35), the elongate member is passed through a spin bath (36) containing a solution of amine oxide and water in which a portion of the amine oxide in the elongate member is leached into the spin bath and the elongate member is then passed through a water bath (38) in which the remainder of the amine oxide is leached out, the refractive index of at least one of the solutions being measured and the concentration of the solution being adjusted if its refractive index varies from a predetermined value by more than a predetermined amount.

2. A method according to Claim 1, characterised in that the refractive index of the dope solution is measured prior to its being extruded and the concentration of the dope is adjusted if the refractive index falls outside the range 1.4890 to 1.4910 at 60°C.

3. A method according to Claim 1 or 2, characterised in that the cellulose, amine oxide and water are pre-mixed to form a solution and the solution is passed through a thin film evaporator (33) to reduce its water content to form the desired dope and the refractive index measurement is carried out on the dope sampled from between the evaporator (33) and the die assembly (34).

4. A method according to Claim 1, 2 or 3, characterised in that amine oxide from the elongate member (35) is recycled from the water bath (38) to the spin bath (36) and the concentration of the amine oxide/water solution passing from the water bath (38) to the spin bath (36) is monitored by refractive index measurements of the solution.

5. A method according to any preceding Claim, characterised in that amine oxide from the spin bath (36) is recycled and used to dissolve more cellulose and the concentration of the amine oxide/water solution passing from the spin bath (36) to be recycled is monitored by refractive index measurements of the solution.

6. A method according to Claim 4 or 5, characterised in that the refractive index of the solution is monitored continuously by an in-line instrument (107, 44) and the monitoring also includes measuring the temperature of the amine oxide/water solution and compensating the refractive index value for temperature variations.

7. A method according to Claim 4, 5 or 6, characterised in that the amine oxide/water solution is passed through an evaporator (45) to reduce its water content before it is passed to the in-line monitoring instrument.

8. A method according to any preceding claim, characterised in that the elongate members are formed as continuous filaments.

9. A method according to any preceding claim, characterised in that the suitability for spinning of a dope of cellulose dissolved in a mixture of amine oxide and water, said dope lying within the boundaries of a ternary diagram for cellulose amine oxide and water being defined by a first line joining the points (85% amine oxide, 15% water, 0% cellulose) (31% cellulose, 0% water, 69% amine oxide), a second line joining the points (78% amine oxide, 22% water, 0% cellulose) (34% cellulose, 66% amine oxide, 0% water), the cellulose base line and the amine oxide base line, is determined by measuring the refractive index of said dope, and determining if said dope has a refractive index lying within a predetermined range.

10. An apparatus for the monitoring of the concentration

of a solution for use in the manufacture of at least one elongate member of solvent-spun cellulose, characterised in that it comprises means (30) to form a hot dope solution from a mixture of cellulose, amine oxide and water, an extruder (34) to form at least one continuous elongate member (35) from the hot dope solution, a spin bath (36) to contain a solution of amine oxide and water through which the elongate member (35) can be passed, a water bath (38) to contain a solution of amine oxide and water through which the elongate member can be passed and monitoring means (40, 107, 44), the monitoring means comprising means to measure the refractive index of at least one of the solutions.

11. An apparatus according to Claim 10, characterised in that it includes an evaporator (33, 45) to apply conditions of heat and reduced pressure to one of the solutions whereby its water content can be reduced.

12. An apparatus according to Claim 11, characterised in that the means to measure the refractive index is a batch means (40) for the hot dope and means (50) are provided to draw off samples of the hot dope between the thin film evaporator (33) and the extruder die (34).

13. An apparatus according to Claim 12, characterised in that the means (40) to measure the refractive index is calibrated to take the measurement at about 60°C and to indicate any measurement of refractive index outside the range 1.4890 to 1.4910.

14. An apparatus according to any one of Claims 10 to 13, characterised in that the monitoring means comprises means (107) to monitor the concentration of the amine oxide/water solution passing from the water bath (38) to the spin bath (36) by measurement of its refractive index.

15. An apparatus according to any one f Claims 10 to 14, characterised in that the monitoring means comprises means

(44) to monitor the concentration of the amine oxide/water solution passing from the spin bath (36) to the means (30) to mix the cellulose, amine oxide and water by measurement of its refractive index.

16. An apparatus according to any one of Claims 10 to 15, characterised in that the monitoring means (107, 44) is coupled to a microprocessor (120, 47) which is programmed to trigger an adjustment to the concentration of the solution if the refractive index value falls outside a predetermined range.

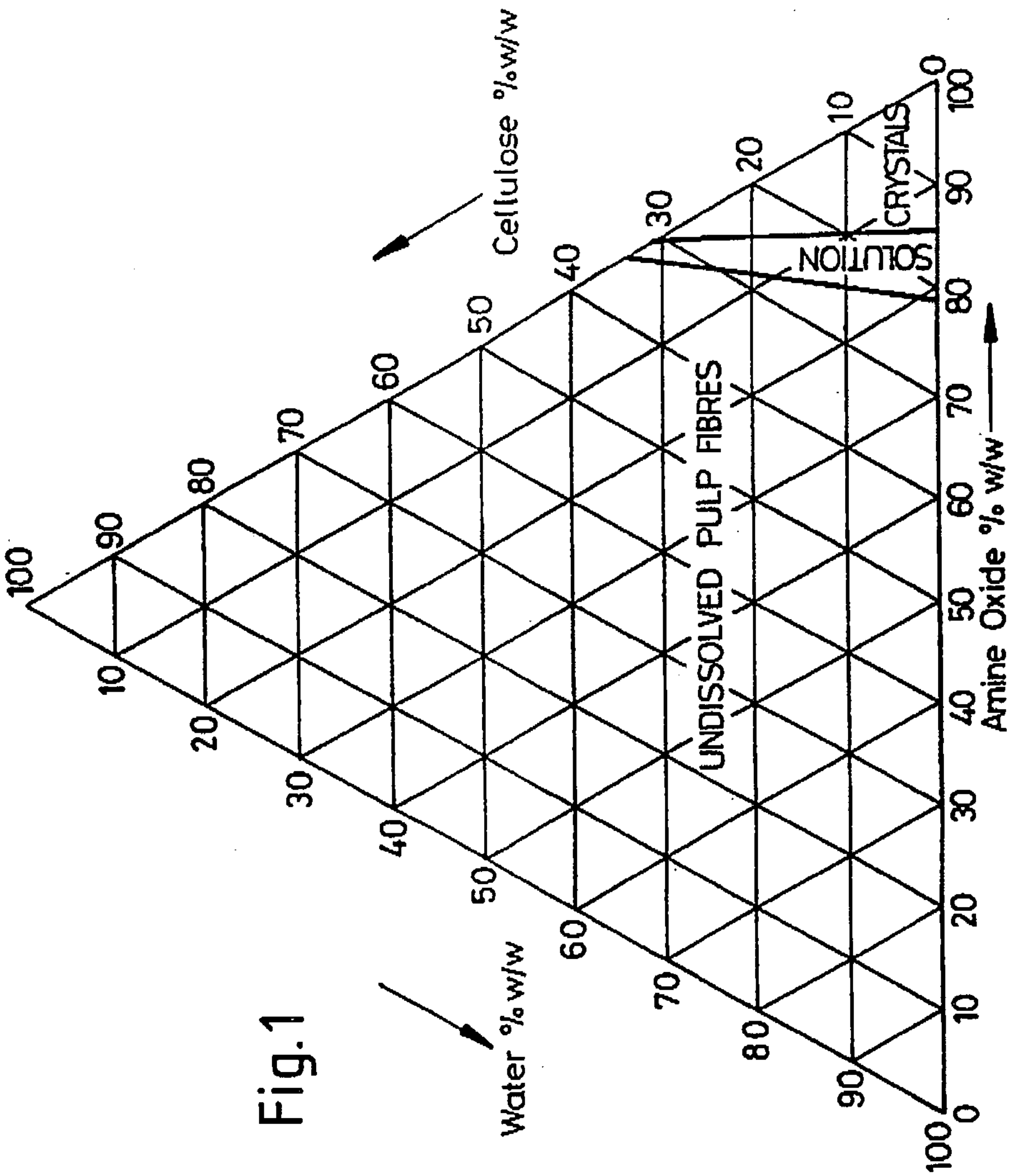
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Fig.1

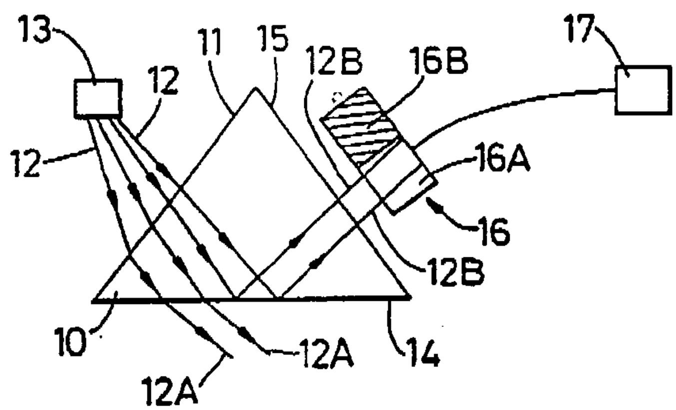
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Fig. 2

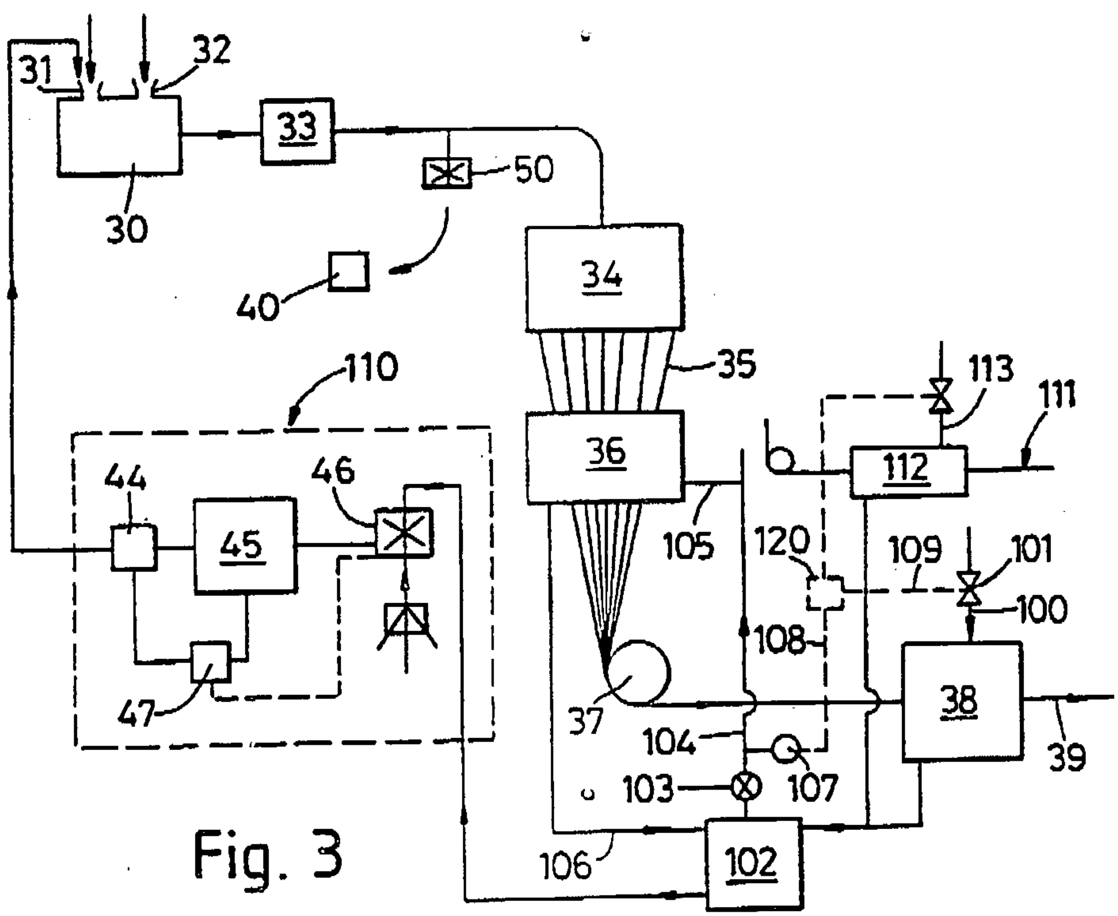
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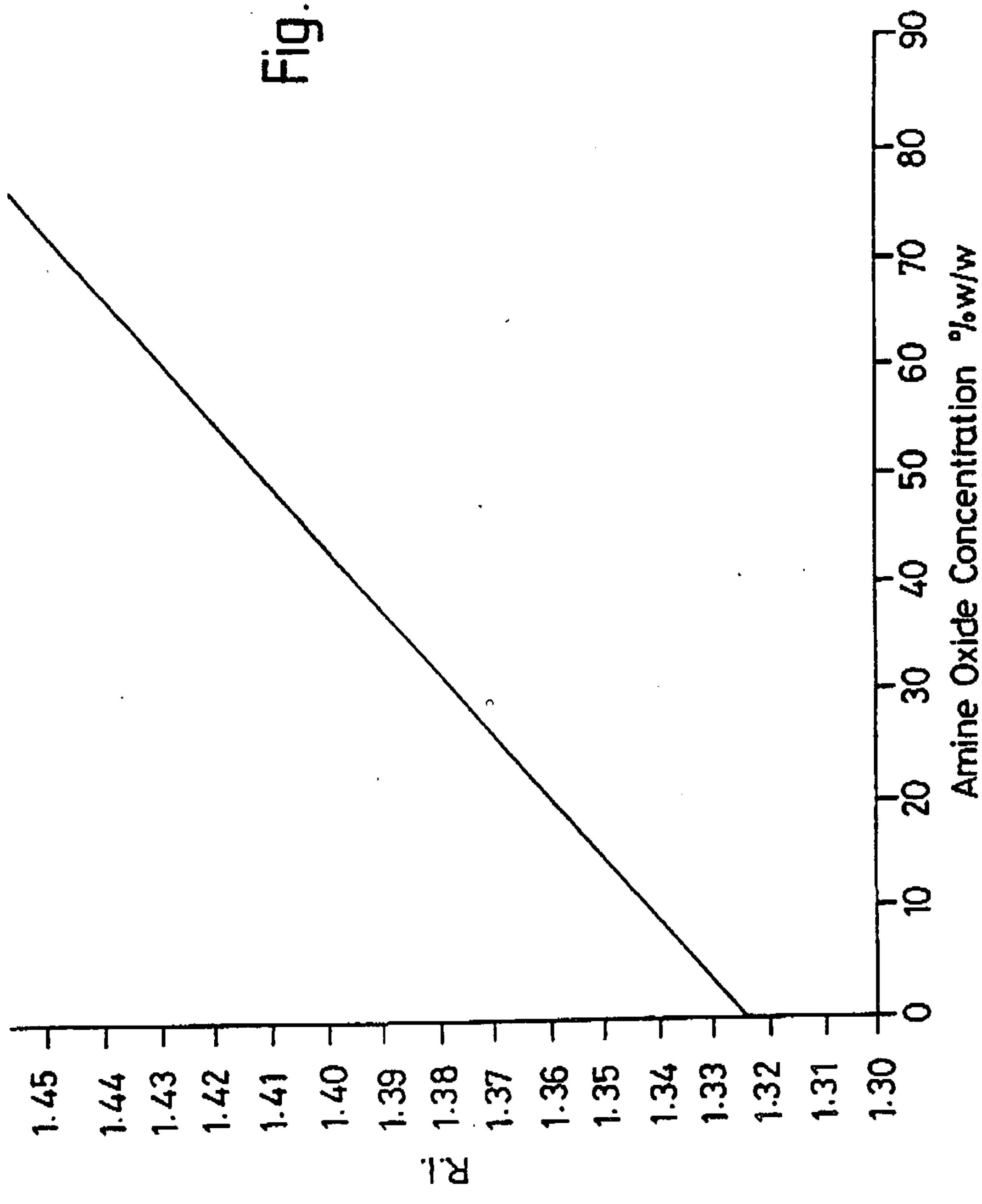
Fig. 3

Fig. 4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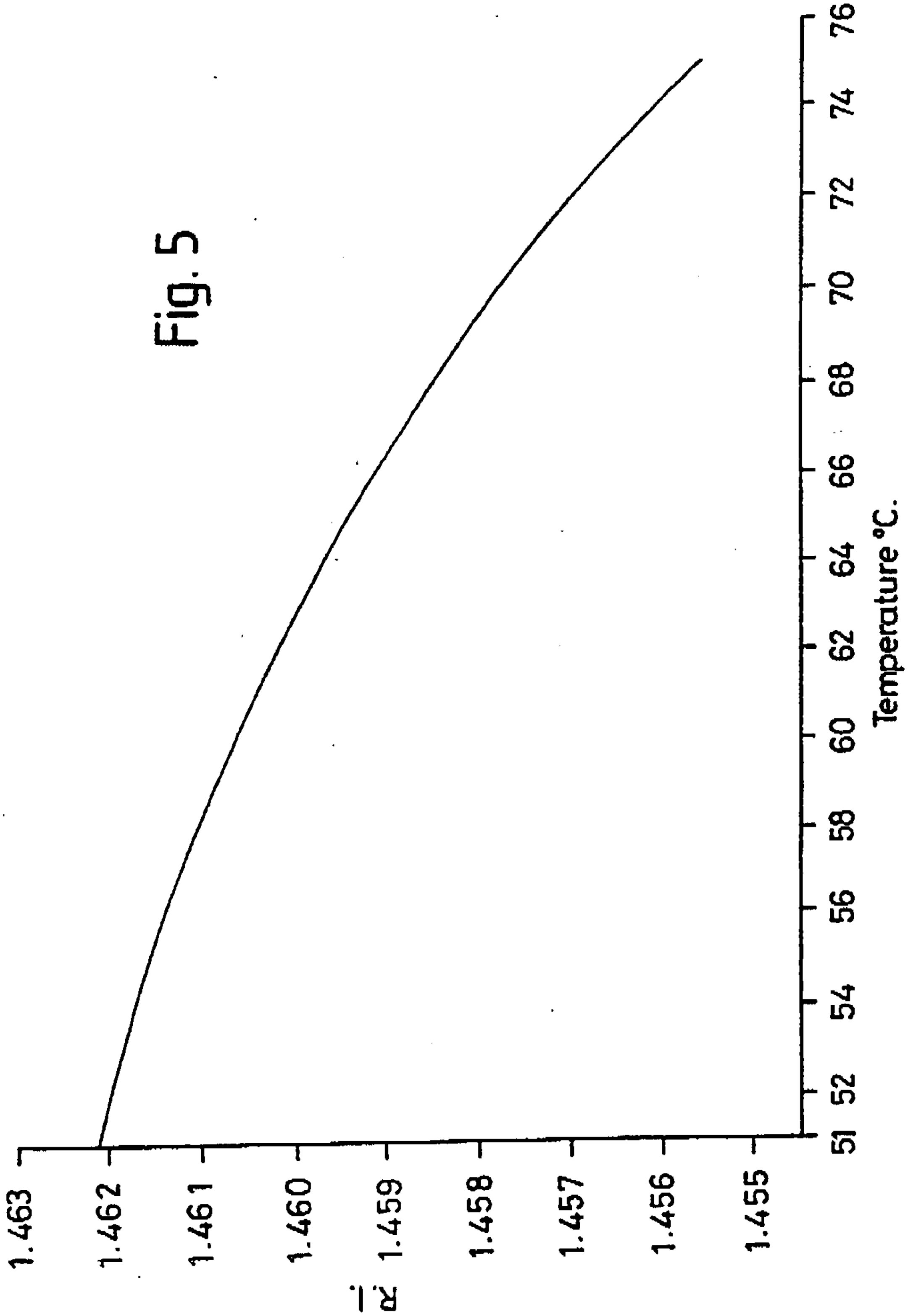
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Temperature °C.

Fig. 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/01090

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 D01F2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 D01F C08L C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 416 698 (CLARENCE C. MCCORSLEY) 22 November 1983 cited in the application ---	
A	PATENT ABSTRACTS OF JAPAN vol. 5, no. 4 (C-038)13 January 1981 & JP,A,55 132 710 (NIPPON ESTER CO LTD) 15 October 1980 see abstract -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
16 September 1994	13. 10. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Tarrida Torrell, J

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 94/01090

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US-A-4416698	22-11-83	US-A-	4246221	20-01-81
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